Synthesis of Cationic Flocculants by the Inverse Microemulsion Copolymerization of Acrylamide with 60% 2-Acryloxyethyltrimethyl Ammonium Chloride in the Monomer Feed. I. Initiation by Ammonium Persulfate/Sodium Disulfite Redox System

F. J. Escudero Sanz,[1*] J. R. Ochoa Gómez,[1] P. M. Sasia,[2] E. Díaz de Apodaca,[1] P. Río[1]

[1]LEIA C.D.T., Sustainable Chemistry Department, Parque Tecnológico de Álava, Leonardo Da Vinci, no 11, 01510 Miñano, Spain
[2]Acideka S.A., Gran Vía 42, 48011 Bilbao, Spain

ABSTRACT: Acrylamide/2-acryloxyethyltrimethyl ammonium chloride copolymers in inverse microemulsion, with a cationic charge density of 60% and a concentration of active matter of 30 wt %, of interest as flocculants have been obtained by inverse microemulsion copolymerization. Interesting inverse microemulsion formulations from both industrial and economical standpoints were selected from pseudoternary phase diagrams. These formulations were polymerized by semicontinuous free radical copolymerization in inverse microemulsion using sodium disulfite and ammonium persulfate as initiators. Influence of initiators and initiator addition conditions (specific flow rate and concentration) on semicontinuous polymerization and final product properties as flocculants have been studied. A strong difference in copolymer solution viscosity has been found when an aqueous solution of sodium disulfite is used as initiator instead of sodium disulfite/ammonium persulfate couple redox, specially for low sodium disulfite solution feeding flow. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2826–2836, 2007

Key words: inverse microemulsion semicontinuous copolymerization; polyelectrolytes; copolymerization; water soluble polymers; flocculants

INTRODUCTION

Currently, most commercial flocculants are acrylamide-based copolymers and they are marketed in three different forms: as solids, as dispersions, and as emulsions.[1] Solid products are hard to use and are usually related to low cost municipal water treatment. Emulsion flocculants are easy to handle products. This kind of products contains polymer concentrations above 30 wt % and emulsifier concentrations below 5 wt %. However, emulsions are thermodynamically unstable and lead to phase separation within a few months. Using microemulsions, which are thermodynamically stable, this problem can be avoided, and low viscosity liquids containing a high concentration of a high molecular weight ($\sim 10^7$ g/mol) polymer could be obtained. The main emulsions advantage over microemulsions is the lower surfactant concentration needed.

Polyelectrolytes could be divided in three different groups depending on their ionic character. Most common polyelectrolytes present in the market are acrylamide-based anionic and cationic copolymers. Cationic copolymers are the most interesting ones from the commercial point of view, due to their higher add value. Nonionic polymers have little application in water treatment processes. Anionic flocculants are mainly used for potable water production or for flocculation of inorganic dispersions and cationic flocculants are typically used for sludge flocculation and dewatering in waste water treatment.

Inverse microemulsion polymerization has been a quite active research subject since the end of the seventies to beginning of the eighties. Up to now, intensive work on microemulsion formulation has been done. In this particular subject, efforts have been made trying to discern whether or not Cohesive Energy Ratio (CER)[2,3] concept may aid in microemulsion formulation development and surfactants blend selection. Most work that have been done, up to now, on inverse microemulsion polymerization

has been devoted to both acrylamide homopolymerization[4–6] and acrylamide–(meth)acrylates copolymerization. Most common comonomers are: alkaline metal acrylates (i.e., sodium acrylate[7]) and methacrylates (i.e., sodium 2-acrylamido-2-methylpropanesulfonate[2] (NaAMPS)) or cationic monomers, such as quaternary ammonium acrylates and methacrylates (i.e., 2-methacryloxyethyltrimethylammonium chloride[8] (MADQUAT, MAETAC)). Inverse microemulsion polymerization mechanisms have been deeply studied using ideal inverse microemulsions. That is, most work has been done on low monomer concentration microemulsions (monomer concentration ranged from 10 to 20 wt %). These studies have mainly focused not only on homo and copolymerization kinetics of acrylamide inverse microemulsions, but also on microemulsion microstructure evolution during all polymerization stages. Final microlatex characterization has been quite useful for polymerization development. Little work has been carried out on high monomer concentration inverse microemulsion polymerization. A few studies has been published in patent literature[9,10] relating inverse microemulsion formulation and polymerization on final properties of microlatices and their application properties.

In this work, we have studied semicontinuous inverse microemulsion polymerization as an alternative technology to emulsion manufacturing for cationic polyelectrolytes of industrial interest, using most industrial common monomers: acrylamide and 2-acryloxyethyltrimethyl ammonium chloride. This work is focused on inverse microemulsions having a monomer concentration higher than 30 wt % with a cationic charge density of 60%. Results of semicontinuous free radical copolymerization in inverse microemulsion using sodium disulfite and ammonium persulfate as initiators are presented, focusing the study on the influence of initiators and initiator addition conditions (specific flow rate and concentration) on semicontinuous copolymerization and final product properties as flocculant.

EXPERIMENTAL

In this paper, all percentages given are by weight (wt %). Charge density is expressed as cationic monomer concentration (wt %) in the initial monomers blend.

Materials

50% Acrylamide aqueous solution (from SNF S.A., France), and 2-acryloxyethyltrimethyl ammonium chloride (ADQUAT; 80% aqueous solution from Atochem, France), were used as received. Microemulsion aqueous phase (APh) consisted of a mixture of both monomers in deionized water (conductivity lower than 10 μS/cm). Pure monomers concentration in aqueous phase is 50% (w/w). Disodium salt of EDTA (from Quimidroga S.A., Spain) was added to complex any metal cation that could inhibit polymerization. Microemulsion oil phase was a mixture 40 : 60 of n-decane and n-tetradecane, whose tradename is Rolling M-245 (Quimidroga S.A., Spain). Both phases were stabilized by an interface of a nonionic surfactant mixture of sorbitan sesquioleate (Crill 43; Croda, UK; HLB = 3.7) and a C_{13} secondary alcohol etoxilated (Softanol 90; Quimidroga S.A., Spain; HLB = 13.3). Ammonium persulfate (APS) and sodium disulfite (SD) (synthesis grade, both from Panreac, Spain) were used as initiators.

Phase diagrams

Fixed quantities of aqueous phase and surfactant system were prepared in different beakers. Mixtures of oil phase and surfactant system of different weight ratios were prepared in 25 mL glass vials. For each blend, a weight sample of aqueous phase is placed in a vial and stirred in a thermostatic bath. Conductivity of both surfactants and oil phase blend and aqueous phase is measured at 25°C. After that, the mixture of oil phase and surfactants is added, drop by drop, over the aqueous phase recording continuously the conductivity. The curve that delineates the macro-microemulsion transition as a function of composition was obtained by direct observation. This transition was observed as a turbid to transparent transition of the blend. The microstructure of microemulsions, globular or bicontinuous, was determined by conductivity. If microemulsion conductivity was higher than 80% of aqueous phase conductivity and liquid was not viscous, we concluded that microemulsion microstructure was globular. If the liquid was not viscous, but its conductivity was lower than 80% of aqueous phase conductivity, microemulsion was considered bicontinuous. Highly viscous microemulsion are usually related to lyotropic microstructures as cubic, hexagonal, or lamellar microstructures.[11]

Polymer synthesis

Aqueous phase is prepared by weighing and its pH may be adjusted by adding a dilute solution of HNO_3. Oil and surfactants are weighed together and mixed with the aqueous phase in a 250 mL volume stirred jacket reactor. Separately, a diluted solution of sodium disulfite should be prepared. Sodium disulfite solution pH must be adjusted with a dilute solution of HNO_3.

Before reaction initiation, microemulsion temperature is adjust to its initial value, and then the reaction mixture is purged with nitrogen for 15 min at

constant flow (4 mL/min at 25°C and 1 bar). Polymerization of microemulsions systems were initiated by adding an aqueous sodium disulfite (SD) diluted solution to a vigorously stirred inverse microemulsion. Nitrogen purge (4 mL/min at 25°C and 1 bar) is kept during all reaction time and sodium disulfite aqueous solution was continuously added at constant flow using a Methrom Dosino 700 dosing unit. Reaction mixture is cooled by water kept at constant temperature. As copolymerization is strongly exothermic, cooling does not allow isothermic reactions. So, the reaction is considered to be finished when temperature goes back to its initial value. Then, both sodium disulfite solution addition and nitrogen purge are stopped.

Inverse microemulsions of cationic copolymers were considered stable if no phase separation after centrifuging for 30 min at 5000 rpm was observed.

General reaction conditions: unless otherwise stated, initial polymerization temperature was 30°C, APS concentration was 0.2% with respect to total amount of monomers, specific flow rate of addition, Q_{sp}, of sodium disulfite aqueous solution was 111.1 mL/kg APh/h with a SD concentration of 0.5%, and total mass of inverse microemulsion was 150 g.

Freeze fracture electron microscopy

Samples were frozen using liquid propane (−188°C) in a LEICA EM CPC equipment and stored in liquid nitrogen (−196°C) up to being processed by cryofracture. Sandwiches produced were cryofractured using a BalTec Baf 060 equipment. Prepared samples were observed using a Jeol 1010 transmission electron microscope with a CCD SIS Megaview III camera. TEM observation was done in high void (10^{-8} mbar) and low temperature (−150°C) conditions.

Viscosity measurements

A solution of 4.5 g of cationic copolymer/L is directly prepared by adding microemulsion, drop by drop, over vigorous agitated deionized water. Solution is kept agitated during 15 min to allow complete microemulsion inversion so that cationic copolymer becomes dissolved into water. Afterwards, viscosity is measured using a Brookfield LVDV-II with LV-1 spindle at 30 rpm and 25°C. Viscosity is expressed as relative viscosity, η_{rel}, with respect to a commercial emulsion of cationic polyacrylamide (tradename: C1596®, Cytec Corp.) of the same charge density as our copolymers.

Acrylamide conversion

A polymer aqueous solution (1 g microemulsion/L) is prepared. It is agitated for 5 min to allow both polymer and unreacted monomers to dissolve. Then,

the solution is vigorously stirred using a high speed mixer at 8000 rpm for 1 min. Afterwards, solution is settled for 5 min to allow bubbles occluded to remove from. Finally, the final solution is prepared by diluting 5 g of solution up to 100 mL using deionized water.

100 μL of the sample are filtered through a 25 μm pore filter and injected into a Water E600 HPLC chromatograph, fitted with two columns in series (Novapack C18 followed by a Fast Fruit Juice column, both from Waters Corp., USA) placed inside an oven thermostated at 55°C and a FID Waters E600 detector set to a wavelength of 200.4 nm. The mobile phase (ultrapure water adjusted at pH 3.5 with H_2SO_4) flow rate was 0.5 mL/min. Running time was 30 min.

This method did not allow the determination of the ADQUAT conversion at a high conversion level. Therefore, the AM conversion was assumed to be similar to the global conversion. As the reactivity ratios for AM and the cationic monomer were 0.61 and 0.475 respectively,[12] and the initial monomer blend concentrations were 0.4 and 0.6 respectively, the monomer blend composition was not strongly modified during the reaction. Chromatography studies on 80% cationic charge density systems (not presented here, as they are beyond the scope of this work), performed with the same monomers, showed that the polymer charge density remained nearly constant during the reaction. It increased slightly in the first polymerisation step and stayed nearly constant up to high conversion levels. When total conversion was achieved, the charge density was the same as that described in the initial blend; when it was not, the density was slightly higher.

Flocculation tests

A solution of 1 g of microemulsion/L is prepared directly by adding microemulsion over stirred water. After 15 min, the solution is ready to be used. Parallel to sample preparation, sludge preparation is also carried out. Sludge should be fresh; otherwise, unrealistic results might be obtained. It must be at room temperature and homogenized. Much care should be taken during homogenization to avoid promoting sludge aerobic digestion.

Comparative flocculation tests were carried out on an anaerobic digested sludge obtained from Vitoria Municipal Water Treatment (Spain) (having the following characteristics, pH = 7.4 and solids concentration = 3.21%). This method determinates the amount of polymer, related to sludge volume, needed to produce flocs strong enough to resist imposed shear, and having good dewatering capacity. To do this, a certain volume of copolymer solution is added to 100 mL of homogenized sludge. The mixture is stirred at 1000 rpm during 10 s using a Triton WRC Stirrer

timer type 131. If after stirring initial sludge is clearly separated in a compact solids aggregate and a clear supernatant, the dose is high enough and may be lowered. If not, the dose should be increased until a clear separation is observed.

RESULTS AND DISCUSSION

Formulation selection

Before polymerization studies, suitable formulations from both technical and economical standpoints should be founded. To attain this objective, pseudo ternary phase diagrams for different HLB values were obtained. All diagrams, obtained as described in experimental part, are displayed in Figure 1. The curve indicates transition between macro (under the curve) and microemulsion (above de curve).

The HLB value determines the macro-microemulsion interface position and so the minimum surfactant concentration needed to achieve a stable microemulsion. The HLB is also related to the maximum concentration of copolymer that can be achieved in the inverse microemulsion and to the self-inverting capacity of microemulsion in contact with sludge slurry. Self-inversion can be described as the capacity of an inverse microemulsion or an inverse emulsion to free and dissolve polymer when placed in contact with water. It is necessary for this kind of products to act as flocculants and it is improved by increasing the HLB value. Figure 2 shows the lowest surfactant blend concentration required to form a microemulsion as a function of HLB for several oil phase/aqueous phase weight ratios. As it can be seen, at HLB 8.75 a microemulsion with the lowest surfactant system concentration is formed; this HLB value is defined as the optimum one. For HLB ranging from 9.0 to 9.5, minimum surfactant concentration necessary to form a microemulsion is nearly constant. For any HLB ranged from 8.75 to 9.5, formulations comprising a surfactant concentration lower than 10% and a monomer concentration higher than 30% could be achieved, which is industrially desirable. Above this range, the system becomes unstable and needs large surfactant concentrations to remain stable, and therefore, monomer concentration in the inverse microemulsion decreases markedly, which is industrially undesirable. As the HLB increases, the weight ratio "hydrophilic surfactant/lipophilic surfactant" of the surfactant blend also increases. This seems to prove that the hydrophilic surfactant, in this case, is less stabilizing than the lipophilic one. It also implies that as this weight ratio increases above a threshold value, the surfactant system becomes much less stabilizing and inverse microemulsion requires a higher surfactant blend concentration to be formed, probably because the higher the hydrophilic character of a surfactant the higher its tendency to be dissolved in the microemulsion aqueous phase, rather than staying at the interface. Then, if a part of the hydrophilic surfactant moves out of the interface, the inversion microemulsion becomes unstable. Consequently, above a certain HLB value microemulsions become unstable.

All stable microemulsions that were formed had a bicontinuous microstructure, rather than a globular one, as determined by conductivity measurements. Preferential formation of bicontinuous microstructure might be justified by Bancroft's rule. In 1913, Bancroft discovered[13,14] that "a hydrophile colloid will tend to make water the dispersing phase while a hydrophobe colloid will tend to make water the dispersed phase." Consequently, interfacial films bends spontaneously towards the phase where the surfactant molecule is more soluble.[15] On this basis, the following application rule[16] was developed: for HLB values below 7 inverse micellar microstructures are favored, and for HLB values above 7 direct micellar microstructures are promoted. HLB values around 7 correspond to the phase inversion region. Transition between both direct and inverse micelle may be abrupt or may pass through a third microstructure. These are normally bicontinuous or lamellar microstructures, which of either plays the role of transition microstructure is a function of interface curvature.[17] It is quite probably that, other than HLB effect, the high monomer concentration in our microemulsions might limit initial microemulsions to be bicontinuous. It had been published that bicontinuous microstructures allow obtaining systems with higher monomer concentration and lower surfactant content in the primary microemulsion,[16] compared with those obtained using globular microstructures.

Owing to this conclusion, first formulation selected to begin with copolymerization tests had a bicontinuous microstructure. This microstructure does not remain all over the polymerization process, but gets modified during polymerization producing final globular systems (see Fig. 3). This conclusion is related to visual microemulsion evolution during polymerization, which coincides with the description of Candau et al.[18] Initial system is a transparent, water like viscosity liquid that turns cloudy and very viscous at the earlier stages of reaction. Usually, some time later (at higher conversion) the system becomes a clear low viscosity liquid, similar to the primary microemulsion.

To carry out copolymerization study the following formulation was selected: 60% of aqueous phase, 30% of oil phase, and 10% of surfactants blend, HLB 9.5, formulation, which gives a cationic copolymer concentration of 30% with a cationic charge density of 60%. Selection was done taking into account indus-
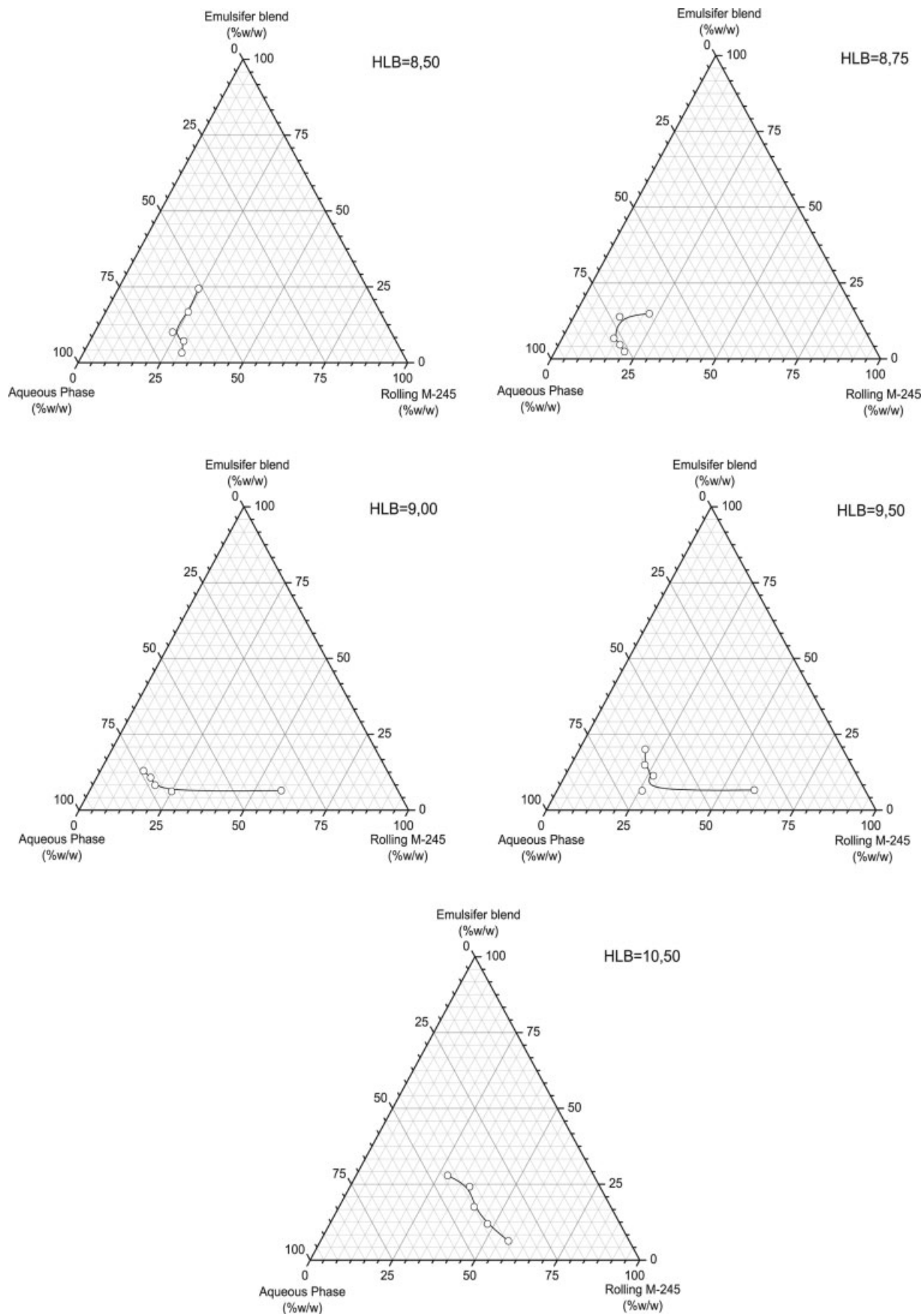
Figure 1 Pseudoternary phase diagrams at 25°C and at different HLBs for a 60% cationic charge density comprising a surfactant blend of Arlacel-83 and Softanol-90, Rolling-M245 as oil phase, and a 50 wt % monomer aqueous solution having an AM/ADQUAT weight ratio of 40/60, as aqueous phase. Lines show the border between macro (below lines) and microemulsion (above lines).
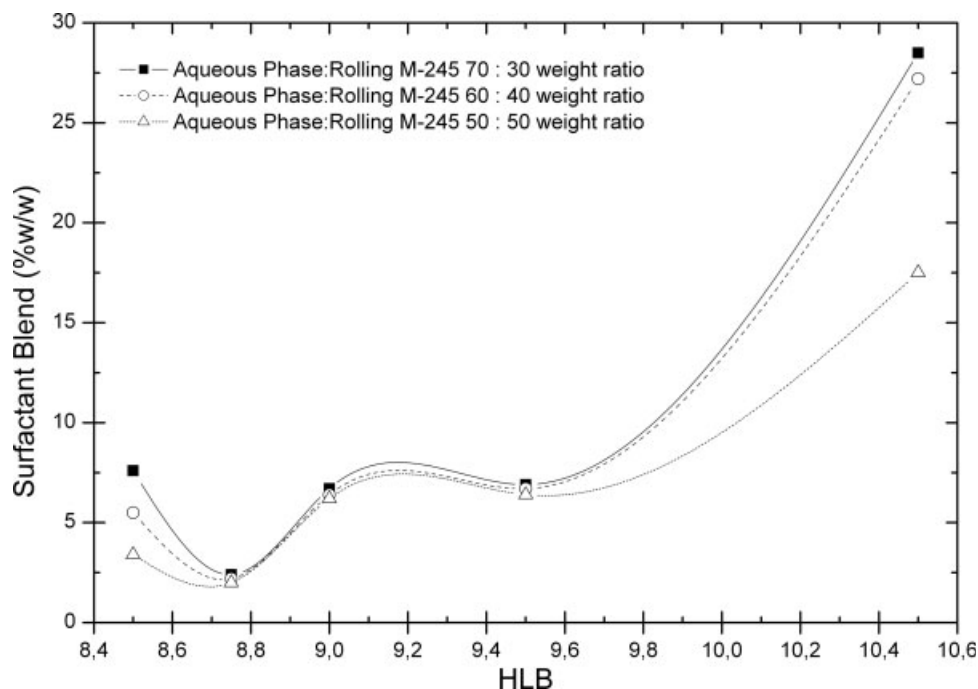
Figure 2 Surfactant system minimum concentration needed to form an inverse microemulsion as a function of HLB for several aqueous phase : oil phase ratios, at 25°C.

trial interest conditions: high solid concentration, low surfactant system concentration, and easy inverting capacity of the microemulsion as it comes into contact with sludge slurry.

Initiation system

A redox initiation system was selected because these systems allow low initiation temperatures. Acrylamide polymerization has a real high polymerization enthalpy (81.5 kJ/mol),[6] and high polymerization temperatures should be avoided. Primary, for security reasons, but also because at temperatures higher than 70°C interimidization reactions, leading to crosslinking,[19] are promoted.

Both components of the redox system were selected from water soluble initiators. This way, the first component can be added to the aqueous phase and a dilute aqueous solution of the second component can be added to the reacting system at constant specific flow rate (ml initiator solution/kg aqueous phase/h). This procedure permits to control copolymer properties, as well as polymerization rate. Ammonium persulfate (APS) and sodium disulfite (SD) were respectively, selected as oxidizing and reducing agents.

Redox system (APS/SD)

The influences of SD aqueous solution specific flow rate (Q_{sp}), SD concentration, and APS concentration in aqueous phase of inverse microemulsion have been studied separately.

Effect of Q_{sp}, for a SD concentration of 0.5% and an APS concentration of 0.2% (both related to aqueous phase mass), on polymerization is plotted in Figure 4. This plot could be divided into two Q_{sp} regions located below and over $Q_{sp} = 66.67$ mL/kg APh/h.

At the lowest Q_{sp} values (55.56 mL/kg APh/h) initiator concentration is quite low and hence, concentration of polymer growing chains will be low. This leads to low values of relative viscosity and
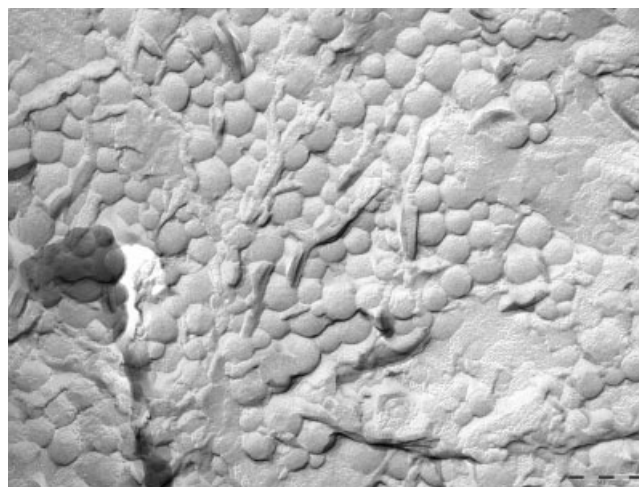

Figure 3 Final microemulsion microphotograph obtained by Cryo Transmission Electron Microscopy (Instrument Magnification 25,000×). Micrographs reveal a reverse micellar system, different from the bicontinuous initial one.
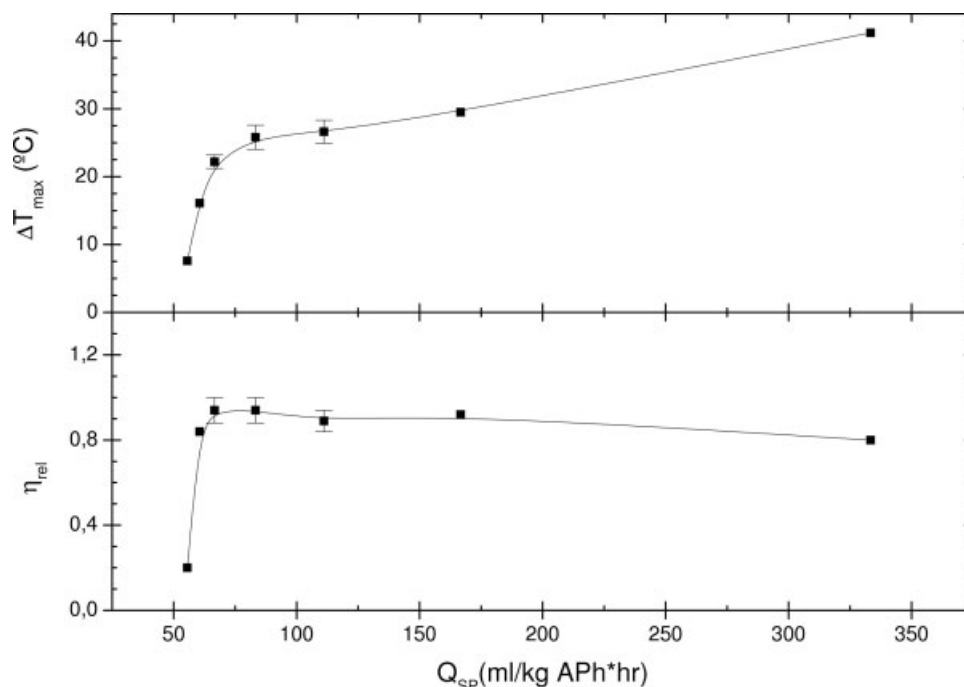
Figure 4 Variation of relative viscosity (η_{rel}) and thermal jump (ΔT_{max}, °C) against specific flow rate of sodium disulfite (Q_{sp}). General reaction conditions: HLB 9.5; Initiation temperature 30°C; SD concentration 0.5 wt %; APS concentration 0.2 wt %.

conversion degree. These results are consistent with low thermal jump values observed. For slightly higher SD specific flows and up to $Q_{sp} = 66.67$ mL/kg APh/h, thermal jump grows up quickly, while η_{rel} remains nearly constant. In this Q_{sp} range (55.56 mL/kg APh/h $\leq Q_{sp} \leq 66.67$ mL/kg APh/h), for a higher Q_{sp} value, both thermal jump and reaction time increase. This could be stated to a conversion increase. In these conditions, a rise of viscosity could also be expected. However, measured viscosity stays constant in this gap. This behavior may be explained by an increase of the number of growing chains, related to a Q_{sp} increase, which leads to products with similar viscosity even if conversion attained is not similar. Same may be supposed for $Q_{sp} > 66.67$ mL/kg APh/h. In this case, η_{rel} still remains constant or decrease slightly, while the thermal jump keeps on increasing slowly and time reaction decreases (from 17 min at 66.67 mL/kg APh/h to 8 min at 333.33 mL/kg APh/h). It may be consider that the number of growing chains are increased significantly for high Q_{sp} values, leading to a reaction speed up and to products having a smaller viscosity.

Similar conclusions could be obtained by studying sodium disulfite solution concentration effect, as can be seen in Figure 5. Relative viscosities are higher than those of SD aqueous solution specific flow rate (Q_{sp}) study at the same SD concentration because of the inclusion in the formulation of a crosslinking agent, N,N^1-methylene-bisacrylamide (MBA). MBA

was added to study the influence of crosslinking on polymer flocculation capacity. Some degree of crosslinking might increase molecular weight, which is positive for flocculation purposes in spite of flocculants are expected to be as linear as possible. On the other hand, crosslinked-branched structures could improve sludge dewatering power of flocculants by reducing the compressibility of the biofloc.[20] The higher viscosities obtained in presence of MBA (compare Fig. 4 with Fig. 5 for 0.5 wt % SD concentration at the same Q_{sp}) seem to indicate the existence of long chain branching. This might be positive as a molecular weight increase is expected. However, flocculation results gave evidence that, in our system, even for low crosslinking agent concentration (20 ppm of MBA related to pure monomers mass for experiments represented in Fig. 5) negatives effects of crosslinking or branching are stronger than positives ones related to higher molecular weight. This could be due to either crosslinking degree introduced by the amount of MBA used is not suitable or structured flocculants are not suitable for the specific sludge used in the flocculation test.

Thermal jump and relative viscosity versus APS concentration in aqueous phase are given in Figure 6. Both parameters are clearly independent of APS concentration indicating that initiation is not produced by a redox mechanism. Consequently, initiation might be directly controlled by sodium disulfite diffusion, although APS might also contribute to
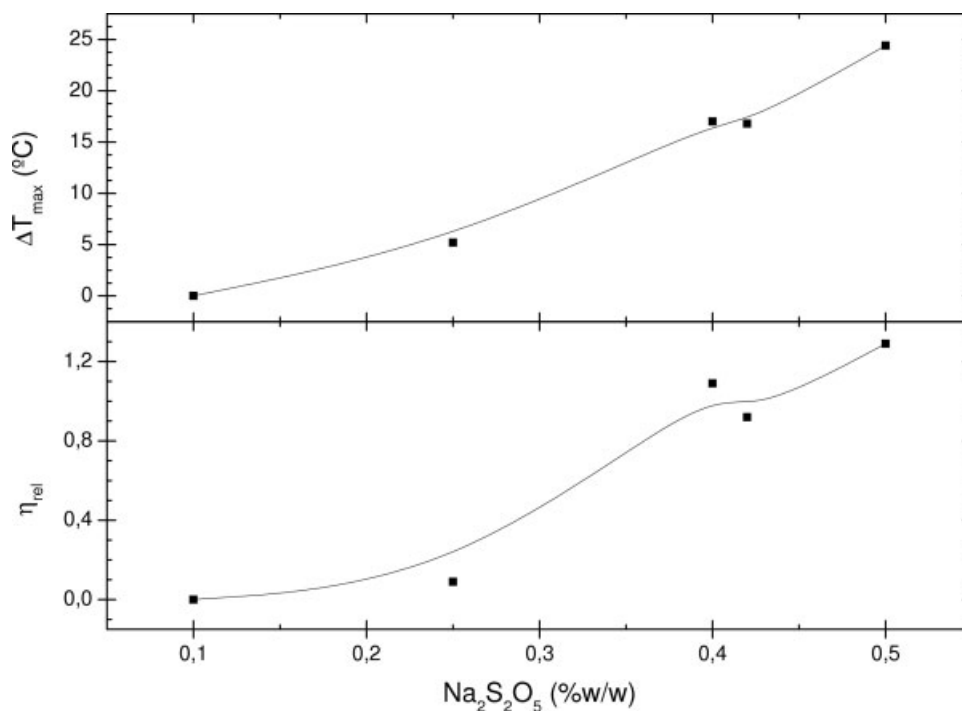
Figure 5 Variation of relative viscosity (η_{rel}) and thermal jump (ΔT_{max}, °C) against sodium disulfite concentration. General reaction conditions: HLB 9.5; Initiation temperature 30°C; APS concentration 0.2 wt %; Q_{sp} 111.11 mL/kg APh/h; N,N^1-methylene-bisacrylamide concentration 20 ppm related to pure monomers.

polymerization as thermal initiator as temperature increases above 40°C during polymerization, giving rise to cationic copolymers of low molecular weight whose contribution to flocculation capacity is null as it is well known from flocculation theory.

Sodium disulfite

As APS does not contributes to redox initiation, to study the influence of SD as the only initiator on polymerization rate and copolymer properties a set of
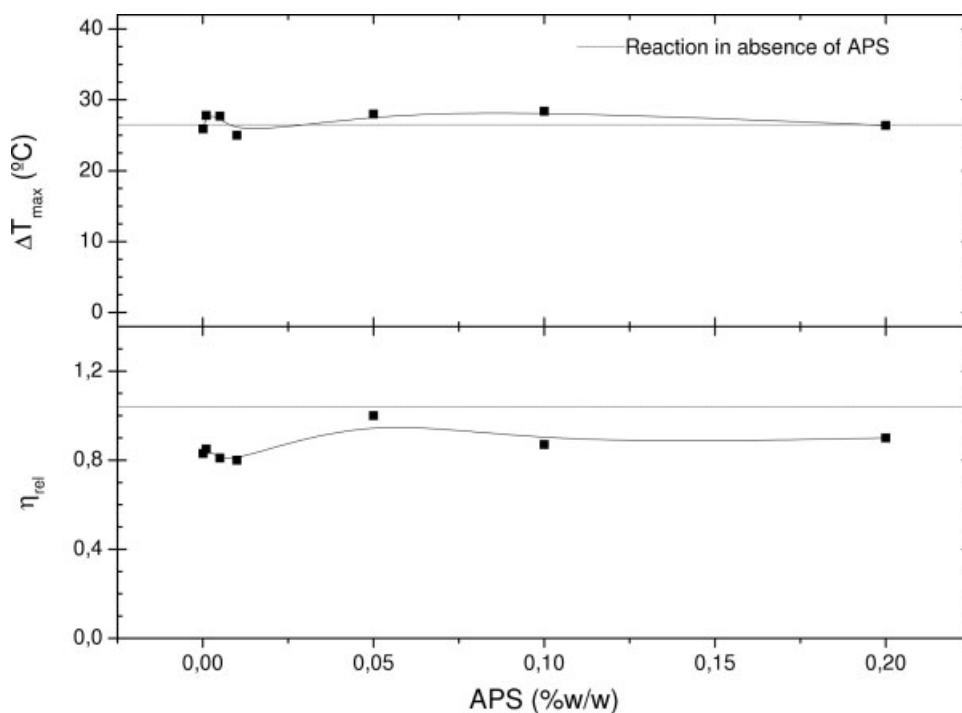

Figure 6 Variation of relative viscosity (η_{rel}) and thermal jump (ΔT_{max}, °C) against APS concentration. General reaction conditions: HLB 9.5; Initiation temperature 30°C; SD concentration 0.5 wt %; Q_{sp} 111.11 mL/kg APh/h.
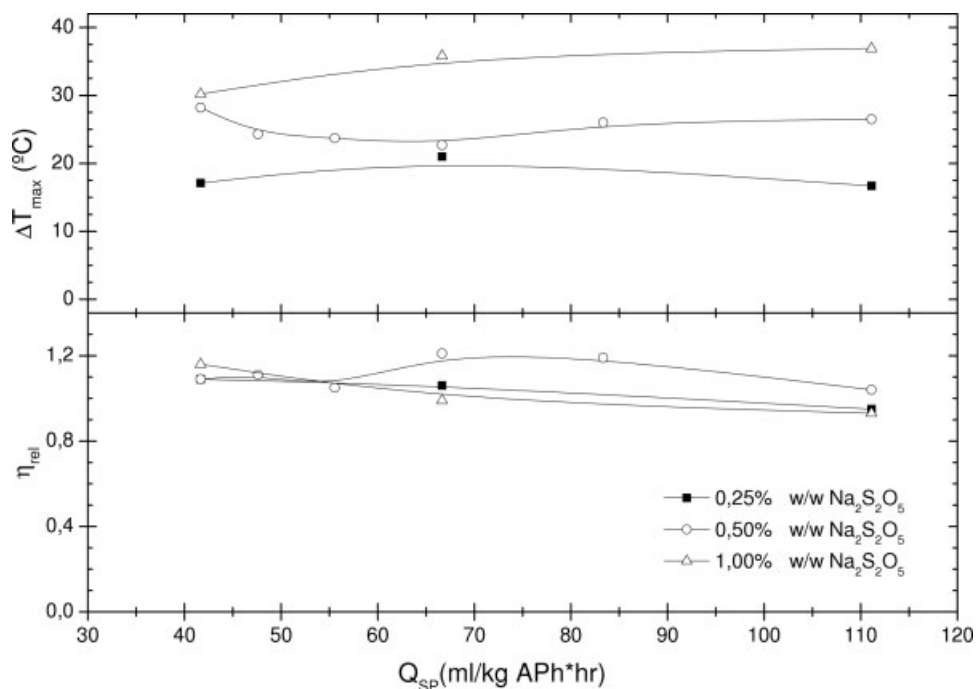
Figure 7 Sodium disulfite initiated copolymerization: sodium disulfite concentration and sodium disulfite specific flow rate Q_{sp} influence on thermal jump (ΔT_{max}, °C) and relative viscosity (η_{rel}). General reaction conditions: HLB 9.5; Initiation temperature 30°C.

experiments removing APS from formulation were carried out. Thermal jumps and relative viscosities for different SD concentrations against Q_{sp} are given in Figure 7.

Comparison of Figures 4 and 7 show differences in the behavior of both systems. In Figure 7 only one region must be considered in the Q_{sp} range studied. For SD system, there is no difference between results
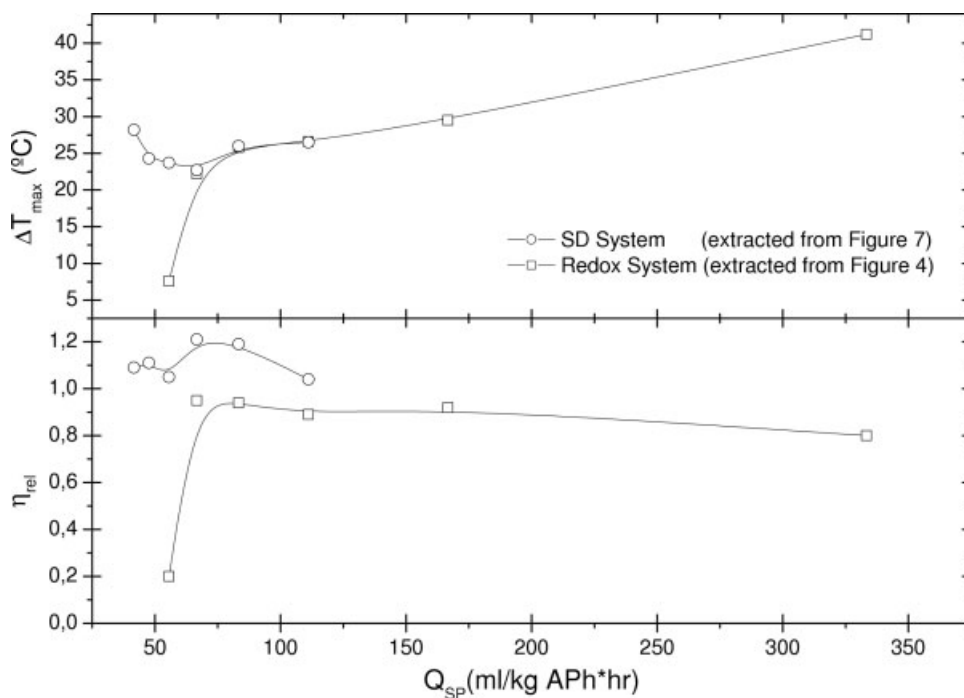

Figure 8 Comparison of polymerization data of copolymerization reactions initiated using the redox system (sodium disulfite/ammonium persulfate) and the ones initiated using sodium disulfite as the only initiator agent. Data are extracted from Figure 4 (SD/APS) and Figure 7(SD). General reaction conditions: HLB 9.5; Initiation temperature 30°C; SD concentration 0.5 wt %; APS concentration 0.2 wt % for redox systems.
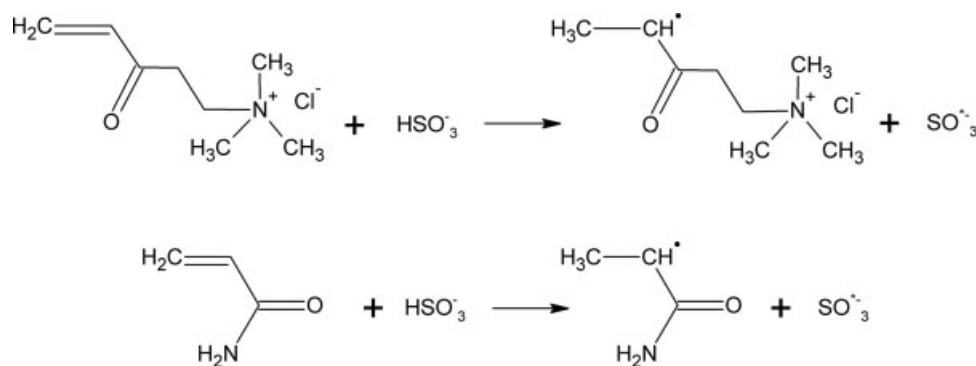
Figure 9 Initiation mechanism proposed by Mukherjee et al.[21] applied to both monomers.

obtained with Q_{sp} above and below 66.67 mL/kg APh/h as can been observed in Figure 7, whereas for APS/DS system for Q_{sp} values below 66.67 mL/kg APh/h, both thermal jump and relative viscosity values decrease quickly. If thermal jump data from Figure 7 for a SD concentration of 0.5 wt % and data from Figure 4 are plotted together (see Fig. 8), it can be seen that thermal jumps for reactions with Q_{sp} between 66.67 and 111.11 mL/kg APh/h for both systems match perfectly, whereas for Q_{sp} values below 66.67 mL/(kg APh/h) both systems behave in a rather different way. If the same is done with relative viscosity values (see Fig. 8), it could be observed that all relative viscosities for SD system are higher than the ones for APS/SD system. When APS is present, for Q_{sp} values below 66.67 mL/kg APh/h high conversions could not be achieved, but when using SD as the only initiator agent, reaction achieves similar thermal jumps at both low and high Q_{sp} values. If we consider that APS is not an inert component of the blend, but it rather acts as a thermal initiator (better above 40°C, but also below 40°C in a less effective way) the small radical concentration produced by the APS may produce oligomers and induce transfer termination reactions. This might justify that for APS/SD systems and Q_{sp} values below 66.67 mL/kg APh/h reaction does not achieve same thermal jumps as for SD system, but for higher Q_{sp} values, radical production is mainly due to SD and high enough to keep reaction living until high monomer conversion is attained. This might also justify a lower molecular weight, and consequently lower relative viscosity for the APS/SD system. When sodium disulfite is used as the only initiator agent, thermal jump increases slightly, and relative viscosity remains nearly constant as Q_{sp} increases for the range studied. The fact that relative viscosities are lower for copolymers obtained using the APS/SD redox system (Fig. 4) than for copolymers obtained using only SD (Fig. 7) could be explained considering that APS only acts as thermal initiator, and low radicals concentration produced by the APS thermal dissociation

(that is rather weak under 40°C) only produce low molecular weight copolymers.

It could also be observed in Figure 7 that there is a strong influence of SD concentration on thermal jump. Doubling SD solution concentration makes thermal jump increase in 10°C. On the other hand, no great difference could be observed on relative viscosity results for same Q_{sp} values and different SD solution concentration. Increasing SD solution concentration, both initiation and polymerization rates are promoted. The higher the initiation rate, the higher the number of chains and consequently the lower the molecular weight, but this effect might be compensated by termination by combination or chain transfer leading to branching that in turn increase molecular weight.

Initiation by sodium bisulfite might be explained by a mechanism based on that proposed by Mukherjee et al.[21] for monomers containing a methyl group attached to vinyl group. These authors proposed that bisulfite ion resulting from sodium disulfite dissociation in water attacks the vinyl group producing radicals in both species (see Fig. 9). They also proposed that both radicals do not recombine just after formed because of steric hindrance imposed by the methyl group attached to vinyl group. But in our case, neither of both monomers have a methyl group that could avoid recombination and, therefore, this lack should be counteracted by resonance stabilization of
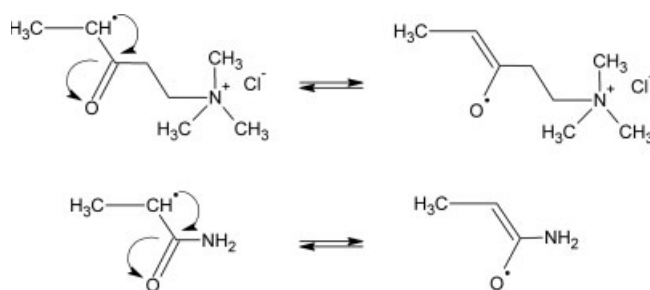

Figure 10 Resonance stabilization of both radicals allowing initiation reaction.

radicals formed by means of the carbonyl group attached to vinyl group, as shown in Figure 10.

CONCLUSIONS

Flocculants having 60% cationic charge density have been obtained by means of inverse semicontinuous microemulsion copolymerization. Pseudoternary phase diagrams have allowed selecting interesting formulations from both technical and economical point of view. By polymerizing on carefully controlled conditions, a formulation comprising an aqueous solution of acrylamide and 2-acryloxyethyltrimethyl ammonium chloride as aqueous phase, a mixture of a C_{13} secondary alcohol etoxilated (Softanol-90) and sorbitan sesquioleate (Crill-43) as surfactant blend, and a mixture of decane and tetradecane as continuous oil phase is possible to obtain inverse microemulsions having a cationic copolymer concentration higher than 30% with a surfactant system concentration as low as 5%, which show a very good sludge dewatering properties. Sodium disulfite has demonstrated being able to initiate polymerization by direct reaction with monomers, having its solution concentration a clear influence on copolymer properties. On the contrary, specific addition flow rate of SD has nearly no influence on copolymer properties. Cationic copolymers obtained by using the APS/SD redox system as initiator have very different viscosities than the ones obtained by using only SD semicontinuously added to the reaction mass as initiator, which can be explained if APS acts only as thermal initiator leading to oligomer formation.

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